The thiosulfate melting at 48° absorbed about 110,000 cal. of heat, and so reduced considerably the rate of temperature increase in the effluent air.

At first, one in every 100 and later one in every 200 of the manufactured canisters was run against 0.5 or one per cent carbon monoxide-air mixtures containing water vapor at a pressure of 14 mm. mercury and at the rate of 32 liters per min. No canister or the lot it represented was accepted which showed a leakage of 0.1 per cent carbon monoxide within 2 hrs.; actually the average life was over 3 hrs. It was found that the higher the temperature the longer the life, which agrees with the fact previously mentioned that Hopcalite is less sensitive to water vapor at higher temperatures. It was further found that the net life of the canister was the same irrespective of whether its use was continuous or intermittent, that is, no deterioration occurred when a partially spent canister was allowed to stand.

ESTIMATED SERVICE TIME IN HOURS FOR HC CARBON MONOXIDE NAVY CANISTER

FOR MEN	Temp. ° F.	Relative Humidity 25%	50%	75%	100%
At Rest	32	60	40	24[1]	18
	50	40	24	16	12
	75	24	12	8	6
	100	12	6	4	3
In Action	32	15	10	6	4.5
	50	10	6	4	3
	75	6	3	2[2]	1.5
	100	3	1.5	1[3]	0.75

[1] Ordinary winter conditions on deck.
[2] Summer conditions on deck.
[3] Engine (boiler) room conditions.

In agreement with the fact that the Hopcalite absorbent functions indefinitely against any concentration of carbon monoxide, provided the effluent air is adequately dried, and hence that the life of the canister is limited solely by the life of the drier, it was found that the net gain in weight of the canister was a sure criterion of its condition. At the time of a breakdown, that is, when the leakage reached 0.1 per cent, as tested by the above-mentioned routine method, the average gain in weight of all canisters was 54 g.; none gained more than 71 g. and none less than 42 g. It was recommended, therefore, that any canister which had gained more than 35 g. above its original weight stamped on the canister should be withdrawn.

Since it is the absorption of water which limits the activity of these canisters, the lower the actual humidity of the air in which the canister is used the longer its life. The accompanying table was, therefore, prepared of the estimated service times of these canisters in use on shipboard under conditions which men both at rest and in action might reasonably encounter.

THE PREPARATION OF ARSENIC TRICHLORIDE FROM WHITE ARSENIC AND PHOSGENE[1]

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INTRODUCTION

At Edgewood Arsenal phosgene was manufactured for use as a war gas by the direct union of carbon monoxide and chlorine in the presence of carbon. It was condensed at about —20° C. under atmospheric pressure, but considerable phosgene was lost in the "tail gas" from the condensers. Means were sought to recover the phosgene in this tail gas and convert it into a commercially valuable product.

It was suggested that this phosgene might be satisfactorily converted into arsenic trichloride by reaction with arsenic trioxide ("white arsenic"). Tests showed that this reaction proceeded very slowly up to the subliming temperatures of arsenic trioxide, and the results were not satisfactory. Experiments made with catalyzers, however, showed that very satisfactory conversion was obtained in the presence of carbon. This paper gives an account of the work done in this connection.

HISTORICAL

The reaction between phosgene and inorganic oxides and sulfides has been studied in detail by Chauvenet.[1] A great number of oxides and sulfides were used, but arsenic was not among them. The reaction was carried out simply by heating the inorganic compound in a tube to a temperature which varied from 300° to 1400° C. according to the material, and passing the phosgene gas over it. Chlorides, and sometimes oxychlorides, were produced, the general reactions being:

$$MO + COCl_2 \longrightarrow MCl_2 + CO_2$$
$$MS + COCl_2 \longrightarrow MCl_2 + COS$$

No catalyzer was used.

Riban,[2] many years before, found that when chlorine is passed over a mixture of tricalcium phosphate and carbon, or when chlorine and carbon monoxide are passed over tricalcium phosphate alone, heated to incipient redness, a small quantity of calcium chloride and *m*-phosphate is formed, but no further change takes place. When, however, carbon monoxide and chlorine together are passed over a heated mixture of calcium phosphate and carbon (boneblack) at 330° to 340° C., $POCl_3$, $CaCl_2$ and CO_2 are produced in quantity. He thought that the carbon acted as a catalyzer by condensing the gases in its pores, and suggested that this reaction might be applied to phosphates in general and to irreducible oxides, like Al_2O_3, from which $AlCl_3$ could be produced. However, he made no experiments using phosgene instead of the mixture of carbon monoxide and chlorine—nor did he attempt to decompose arsenic compounds.

EXPERIMENTAL

LABORATORY EXPERIMENTS—Experiments were made in the laboratory as follows:

Phosgene (analyzing 99.7 per cent $COCl_2$), from a small tank, was dried with sulfuric acid, measured in a flow meter (calibrated for phosgene), and then mixed with air which had been dried and metered in a similar manner. The resulting mixture was run through a Pyrex glass tube containing the charge, generally a mixture of white arsenic and carbon. The tube was heated in an electric oven, and the temperature measured by a long thermometer which

[1] This article has been approved for publication by Major-General William L. Sibert, Director of the Chemical Warfare Service, U. S. A.

[1] *Compt. rend.*, **152** (1911), 87, 1250; Barlot and Chauvenet, *Ibid.*, **157** (1913), 1153.

[2] *Ibid.*, **95** (1882), 1160; **157** (1913), 1432.

reached to the center of the charge inside the tube. The arsenic trichloride formed was collected in a receiver and the exit gases run to waste through a reflux condenser. The charge was prepared from dry materials, but at the beginning of each experiment dry air was passed through the heated tube in order to drive out any remaining traces of moisture.

The phosgene and carbon dioxide in the ingoing and outgoing gas were determined by analyses made on a measured volume of gas collected over mercury. The $COCl_2$ and CO_2 were absorbed in one per cent aqueous sodium hydroxide and the contraction in volume noted; the volume of the $COCl_2$ was calculated from the chloride content of the solution, as determined by titration (Mohr's method) after neutralization with normal nitric acid; the CO_2 was obtained by difference. Analysis of known mixtures gave satisfactory results.

Table I gives a summary of the results obtained in different experiments, each of which was run for about 5 hrs. Very concordant analyses were obtained in each test. It was found that the reaction did not proceed well at low temperatures, and a temperature of 200° C. was therefore used.

TABLE I—LABORATORY TESTS OF THE REACTION BETWEEN PHOSGENE AND WHITE ARSENIC

Temperature, 200° C.
Tube, 1.7 cm. internal diameter
Length of charge, 30 cm.[1]

	Charge (per cent by weight)		Ingoing Gas (cc. per min.)		Outgoing Gas (per cent by volume)	
TEST NO.	As_2O_3	Carbon[2]	$COCl_2$	Air	$COCl_2$	CO_2
21	100	0	5	0	43.1	45.0
15	80	20	5	0	0.5	95.0
19	80	20	5	20	2.8	17.5
20[1]	80	20	5	20	0.2	20.9

[1] For Test 20 the tube was completely filled with the charge for a distance of 40 cm. In the other tests the carbon and white arsenic were ground together. For this test a mixture of As_2O_3 with 1/8 in. pieces of carbon, was used.

[2] A variety of carbon know commercially as "filt-char" was used for most of the tests.

The arsenic trichloride produced was water-white and pure, except that it contained a small quantity of dissolved phosgene.[1] With a proper rate of gas flow, the phosgene in phosgene-air mixtures was almost completely removed.

PLANT EXPERIMENTS—An apparatus very similar to the one used in the laboratory, but built of iron pipe was used for small scale works experiments. The furnace was made from a 5-ft. length of 4-in. pipe and was electrically heated by a resistance ribbon winding, and insulated with magnesia asbestos pipe covering. The caps at the ends of the pipe were drilled and threaded for inlet and outlet, respectively, and each contained a thermometer well. The temperature was controlled by a water rheostat in the electric circuit. A water-cooled condenser with a trap and a receiver was attached to the exit end of the furnace. The apparatus was operated by suction; "tail gas" from the phosgene plant condensers was drawn in succession through a flow meter, through the furnace containing the charge, through the condenser and the trap. Sampling cocks were placed on the inlet and outlet lines.

The entering and exit gas was analyzed from time to time for phosgene and carbon dioxide, as previously described. An average tail gas entering the apparatus contained 35 per cent $COCl_2$. Carbon monoxide, carbon dioxide and traces of chlorine and water vapor were also present. Although no tests were made for hydrochloric acid, it is probable that a small amount was present.

The condensate separated in two layers, arsenic trichloride below and water on top, both being colored red-brown by iron. The iron in the $AsCl_3$ was determined colorimetrically.[1] The water layer was analyzed for arsenic and iron gravimetrically, and for chloride by Volhard's method. The arsenic and iron were calculated as chlorides, the residual chloride as hydrochloric acid, and the rest of the sample assumed to be water.

The results of the experiments with a charge containing by weight 80 per cent As_2O_3 and 20 per cent filt-char are given in Table II:

TABLE II—EXPERIMENTS WITH SMALL SCALE WORKS APPARATUS FOR ARSENIC TRICHLORIDE FROM PHOSGENE TAIL GAS

Charge, 80 per cent As_2O_3 and 20 per cent filt-char

Test Number	3	4*b*	4*c*	5*a*	5*b*
Duration of Experiment (hrs.)	4.25	4.5	2	3	2
Average Temp. (° C.)	200	200	260	260	260
Rate Ingoing Gas (cu. ft. per min.)	0.10	0.05	0.05	0.05	0.10
Average per cent $COCl_2$ in Ingoing Gas	33	39	37	38	38
Average per cent $COCl_2$ in Exit Gas	16	10	1.3	0.7	15
G. $COCl_2$ Used up per hr.	117		110	128	159
Theoretical g. $AsCl_3$ per hr.	143		134	156	194
Actual g. $AsCl_3$ per hr.	106		113	121	146
Per cent Yield	74		85	78	75
G. Water Layer per hr.	25		25	13	19

The weight of the arsenic trichloride was obtained after separation from the water layer with a separatory funnel. An average sample contained 0.05 g. of iron per liter, and a small amount of dissolved phosgene.

A typical analysis of the water layer was:

$AsCl_3$	35.3 per cent
HCl	14.6 per cent
$FeCl_3$	0.8 per cent
H_2O (by difference)	49.3 per cent

The yields obtained were remarkably good, especially since the calculation was based on the average chloride content of the ingoing gas. Quite a little more arsenic trichloride would have been obtained had there been no water layer in the condensate. No arsenic or arsenic trioxide sublimed out of the furnace, although the filt-char was found to be bound together in lumps, when the furnace was opened. No loose, white arsenic was left.

A few experiments made with this furnace using pure phosgene mixed with air gave a condensate containing very little water and iron, showing that a much purer product could be made by purifying and drying the tail gas before introducing it into the furnace.

SUMMARY AND EXTENSION

1—Arsenic trichloride can be prepared from white arsenic and phosgene at temperatures above 175° C. in the presence of carbon, which acts as a catalyzer.

2—This reaction has been successfully carried out at 200° to 260° C., using pure phosgene in a glass apparatus, and impure "tail gas" from phosgene manufacture in a small scale works apparatus built of iron

[1] The solubility of phosgene in arsenic trichloride was determined by R. E. Hall and N. W. Rakestraw, of the Edgewood Arsenal Chemical Laboratory.

[1] By a method developed at the Edgewood Arsenal Chemical Laboratory by J. A. Wilkinson and W. T. Schrenk.

pipe. The yields were almost quantitative. The product made in the laboratory was water-white and pure except for dissolved phosgene. The condensate from the works apparatus separated into two layers—water, and arsenic trichloride—which contained a small amount of iron in addition to dissolved phosgene. Some arsenic trichloride was lost in the water layer, but preliminary purification of the tail-gas would materially reduce this loss.

3—The method of chlorination used in this work, namely, the treatment of inorganic compounds with phosgene in the presence of carbon as a catalyzer, will probably be of general application, and may make it possible to satisfactorily chlorinate inorganic compounds with phosgene at lower temperatures than has heretofore been possible. Commercially, a number of different types of furnaces, intermittent or continuous, could be used for these reactions.

ACKNOWLEDGMENT

In conclusion it is desired to express appreciation of the kind assistance and suggestions from Major W. L. Evans, of the Edgewood Arsenal Chemical Laboratory, and Majors F. C. Frary and Sterling Temple, of the Edgewood Arsenal Chemical Plants.

THE CHEMICAL INDUSTRY AND TRADE OF SPAIN

By O. P. Hopkins, Washington, D. C.

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The wealth of Spain lies chiefly in her agriculture and in her mineral resources. Of the products that may be called agricultural, and which enter into trade, the best known examples are olive oil, wines, citrus fruits, and nuts. The minerals recovered in the most important quantities are iron, coal, copper, iron pyrites, lead, mercury, zinc, and salt. Cotton textiles are the outstanding product of industrial manufacture.

Although one of the oldest nations in Europe, the Spanish people have not made great progress in developing their resources. At the time the war broke out the domestic production of food was insufficient to meet the home demand, coal was largely imported from England while the domestic supply was much neglected, metallic ores were shipped out of the country in immense quantities for others to refine and work, the water power was utilized to only a limited extent, fertilizers were imported ready-made, and so on. Much of the olive oil and wines exported required further refining and blending. Only a few really finished products were shipped out of the country.

In spite of its many disadvantages to Spain, the war has served to change these conditions rather radically. Attention has been focused on the necessity of producing more food at home, for rations were short while hostilities were on. Even olive oil exports were taboo part of the time. The importance of fertilizers is now recognized, and steps have been taken to increase the domestic output, especially of ammonium sulfate. Enough Spanish coal is mined to meet home demands, which run about 7,000,000 tons a year. The developments in mining and metallurgical fields have been more striking than in any other, under the direct stimulus of war demands, and it is considered certain that from now on more and more minerals will be recovered and a much larger percentage refined in Spain.

Special attention has of late been given to hydro-electric development, for which there is considered to be a great future. In 1918 more than 400,000 horse-power was produced by plants having a potential capacity of nearly a million horse power. It is planned to utilize such power more largely in the future for the production of needed alkalies and ammonium sulfate, and in the metallurgical industries.

Trade between the United States and Spain before the war was not comparatively important, and few articles were involved that can be classified as chemical or allied products. It was largely a matter of exchanging American cotton, with some tobacco, mineral oil, electrical equipment, and lumber, for Spanish copper, cork, pyrites, fruits, nuts, and olive oil. The war hindered rather than helped trade, but the enrichment of Spain through the war will probably mean larger purchases from the United States, and, in the end, larger sales to us.

The statistics prepared for this article will show the point to which Spanish chemical industries and trade had developed when the war came and the manner in which the war affected them.

PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS

Official statistics of production are concerned almost exclusively with products of mineral origin. To present a more complete picture of the industries, therefore, some notes have been prepared from various reliable sources, chiefly from material published by the Bureau of Foreign and Domestic Commerce, as follows:

Extensive deposits of potash were discovered as long ago as 1911 in Catalonia, but no definite action was taken toward working them until December 1918, when the government announced conditions under which concessions would be made. A number of explanations are offered to account for the delay in starting production, and charges are made from some quarters that the German syndicate was successful for many years in delaying operations. The government now has entire control of the situation. The first concession was granted to a Belgian company, and an American company has also entered the field. There are no figures of production available.

The manufacture of licorice extract and paste is an important Spanish industry, but there are no statistics of production. This is a comparatively new industry,